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GEOQUÌMICO: An Interactive Tool for Comparing Sorption Conceptual Models (Surface Complexation Modeling versus K_D)

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Abstract

Within reactive geochemical transport, several conceptual models exist for simulating sorption processes in the subsurface. Historically, the K_D approach has been the method of choice due to ease of implementation within a reactive transport model and straightforward comparison with experimental data. However, for modeling complex sorption phenomenon (e.g. sorption of radionuclides onto mineral surfaces), this approach does not systematically account for variations in location, time, or chemical conditions, and more sophisticated methods such as a surface complexation model (SCM) must be utilized. It is critical to determine which conceptual model to use; that is, when the material variation becomes important to regulatory decisions. The geochemical transport tool GEOQUÌMICO has been developed to assist in this decision-making process. GEOQUÌMICO provides a user-friendly framework for comparing the accuracy and performance of sorption conceptual models. The model currently supports the K_D and SCM conceptual models. The code is written in the object-oriented Java programming language to facilitate model development and improve code portability. The basic theory underlying geochemical transport and the sorption conceptual models noted above is presented in this report. Explanations are provided of how these physicochemical processes are instrumented in GEOQUÌMICO and a brief verification study comparing GEOQUÌMICO results to data found in the literature is given.

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Abbreviations

ADR	advection-dispersion-reaction
API	application programming interface
GUI	graphical user interface
MCL	maximum contaminant level
NRC	U.S. Nuclear Regulatory Commission
PNG	portable network graphics
SCM	surface complexation model
SNL	Sandia National Laboratories
TVD	total variation diminishing

1. Introduction

Within the realm of subsurface geochemical transport, numerical modeling provides a means by which researchers may better understand coupled physicochemical processes and develop methodologies for predicting fate and transport of contaminants. Modern geochemical transport models are highly sophisticated tools for simulating the transport of large numbers of chemical components that interact through complex nonlinear reactions. These models rely on extensive characterizations of the subsurface both in the field and in the laboratory, without which simulation results would be unfounded. Even with the immense amounts of data provided by characterizations, parameter uncertainty is still a major concern. Scientists have studied parameter uncertainty for years and have developed techniques such as stochastic approaches to modeling flow and transport to address such dilemmas. However, little has been mentioned of conceptual model uncertainty until recently (Bredehoeft, 2005). Of particular concern to regulatory agencies such as the U.S. Nuclear Regulatory Commission (NRC), is the uncertainty associated with radionuclide sorption mechanisms.

Historically, the conceptual model of choice for sorption has been the linear K_D , which has been shown to potentially misrepresent sorption processes within radionuclide transport (Bethke and Brady, 2000). Ridge et al. (2005) discuss the advantages of thermodynamic sorption models in reactive transport modeling as an alternative to the K_D approach. The thermodynamic sorption models may require additional data collection and their use may be practical for only some sites. To facilitate licensing decisions on the choice of appropriate sorption models, a one-dimensional, web-based geochemical transport model or tool has been developed to compare and contrast sorption modeling techniques. The model focuses on providing the NRC licensee with the geochemical transport capabilities necessary to compare the ubiquitous K_D approach to more sophisticated surface complexation modeling (SCM) techniques. The model is fully customizable, and the end user can adjust transport and geochemical parameters as he or she desires using a graphical user interface (GUI). Furthermore, NRC staff can develop preconfigured reactive transport scenarios with prescribed geochemical and/or transport parameters. This tool will facilitate the decision-making process, providing NRC staff and licensees with a simplified geochemical transport tool tailored around site-specific phenomenon and executed using a straightforward user-friendly interface. Staff and licensees can perform a comparison between the K_D approach and SCM to determine whether further characterization is necessary for SCM.

The purpose of this report is to document the prototypical web-based geochemical transport tool GEOQUIMICO developed for the NRC by Sandia National Laboratories. The report first provides theoretical detail on geochemical transport as it is applied to modeling sorption processes. The graphical user interface is then presented with illustrations of its useful features. Results from a study where GEOQUIMICO was compared with modeling data from Bethke and Brady (2000) is also included. Finally, future directions for further model development in order to provide the NRC with more utility are presented.

2. Theoretical Background

The generalized governing equation for reactive transport, also known as the advection-dispersion-reaction (ADR) equation is

$$(1) \quad \frac{\partial(\phi\Omega_i)}{\partial t} - \nabla \cdot (\phi D \nabla \psi_i - \nu \psi_i) = R_i(c_1, c_2, \dots, c_{N_c}) + S_i(\psi_i),$$

where kinetic reaction rates (R) are based on the free ion concentrations of the primary or basis species in the system (c), and advection (ν), dispersion (D) and sources/sinks (S) are computed as a function of the total aqueous component concentrations (ψ) of the N_c primary species in the system. Ω represents the total component concentrations (i.e. sorbed and aqueous) which is used within the accumulation term or time derivative in this equation to account for change in concentration or mass in both the aqueous and sorbed phases over time. It should be noted that we assume constant porosity (ϕ).

Since currently GEOQUIMICO considers solely equilibrium formulations for reactive transport based on the local equilibrium assumption (Rubin, 1983), the kinetic reaction term (R) is dropped from the governing equation for the purposes of this work. Regarding the sources/sinks term (S), sorption processes could be implemented as a source/sink within the transport system. However, this approach would require a kinetic formulation, and incorporating sorption within the accumulation term, i.e.

$$\frac{\partial(\phi\Omega_i)}{\partial t}$$

is much more straightforward. Therefore, the sources/sinks term is also dropped and Equation 1 takes the form

$$(2) \quad \frac{\partial(\phi\Omega_i)}{\partial t} - \nabla \cdot (\phi D \nabla \psi_i - \nu \psi_i) = 0.$$

At this point it is important to differentiate between total aqueous, total sorbed, and total component concentrations, defined as ψ , $\bar{\chi}$, and Ω , respectively. The total aqueous concentration of component i (ψ_i) is computed as the sum of the component's aqueous free ion concentration (c_i) and its stoichiometric contribution (a_{ij}) to each of the N_x aqueous complexes or secondary species (X) in the system, as defined by Lichtner (1985),

$$(3) \quad \psi_i = c_i + \sum_{j=1}^{N_x} a_{ij} X_j.$$

Aqueous complex concentrations are computed as a function of their equilibrium constant (K_{eq}) and the free ion concentrations

$$(4) \quad X_j = K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{ij}}.$$

By substituting Equation 4 into Equation 3, the total aqueous component concentrations may be computed as a function of the free ion concentrations in the system

$$(5) \quad \psi_i = c_i + \sum_{j=1}^{N_x} a_{ij} K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{ij}}.$$

Regarding total sorbed component concentration, we must differentiate between sorption through a K_D model and surface complexation model. In the case of a K_D model, sorption is defined by a distribution coefficient or K_D , which is a ratio of sorbed concentration (\bar{S}) to aqueous concentration (in this work, overbars indicate species in the sorbed phase)

$$(6) \quad K_D = \frac{\bar{S}}{c}.$$

Therefore, the sorbed concentration is defined as

$$(7) \quad \bar{S}_i = K_{D,i} c_i \quad i = 1, 2, \dots, N_c,$$

where the units of \bar{S} are moles per kg rock/soil as apposed to moles per liter of solution, the units of c . In order to convert these units to units consistent with aqueous concentration, Equation 7 must be scaled by the rock/soil bulk density (ρ_b) and porosity (ϕ) resulting in an equivalent aqueous concentration (\bar{c}_s)

$$(8) \quad \bar{c}_{s,i} = \frac{\rho_b}{\phi} \bar{S}_i = \frac{\rho_b}{\phi} K_{D,i} c_i \quad i = 1, 2, \dots, N_c.$$

To keep this formulation general, it is assumed that for components not sorbing through the K_D approach, the value of K_D is set to zero.

The approach to computing sorbed concentrations through the surface complexation model is very similar to that of the aqueous complex. Surface complex concentrations (\bar{X}) are computed as a function of an equilibrium constant (\bar{K}_{eq}), a nonlinear Boltzmann factor

$$\exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right),$$

and the free ion and sorption site concentrations (s), the site concentrations being calculated as a function of the mineral surface area and the site density

$$(9) \quad \bar{X}_m = \bar{K}_{eq,m} \exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right) \prod_{k=1}^{N_c} c_k^{a_{im}} \prod_{n=1}^{N_{site}} s_n^{a_{nm}} \quad m = 1, 2, \dots, N_s.$$

Here, the Boltzman factor is an exponential function of Δz (change in surface charge), Ψ (surface potential), F (Faraday constant), R (gas constant) and T_K (absolute temperature), and accounts for electrostatic effects on the equilibrium constant. The use of this factor will be discussed later.

The total sorbed component concentration of component i ($\bar{\chi}_i$) is computed as a sum of its stoichiometric contribution (a_{im}) to each of the N_s surface complexes (\bar{X}) in the system and/or its contribution to sorption through the K_D approach

$$(10) \quad \bar{\chi}_i = \sum_{m=1}^{N_s} a_{im} \bar{X}_m + \bar{c}_{s,i} \quad i = 1, 2, \dots, N_c.$$

Although GEOQUIMICO is algorithmically capable of modeling both processes simultaneously, it is most likely that the modeler would choose to simulate one or the other.

Substituting Equations 8 and 9 into Equation 10, we obtain the total sorbed concentration for component i solely as a function of free ion and site concentrations

$$(11) \quad \bar{\chi}_i = \sum_{m=1}^{N_s} a_{im} \bar{K}_{eq,m} \exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right) \prod_{k=1}^{N_c} c_k^{a_{im}} \prod_{n=1}^{N_{site}} s_n^{a_{nm}} + \frac{\rho_b}{\phi} K_{D,i} c_i \quad i = 1, 2, \dots, N_c.$$

Finally, the total concentration for chemical component i is defined as the sum of Equations 5 and 11

$$(12) \quad \Omega_i = c_i + \sum_{j=1}^{N_s} a_{ij} K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{kj}} + \sum_{m=1}^{N_s} a_{im} \bar{K}_{eq,m} \exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right) \prod_{k=1}^{N_c} c_k^{a_{im}} \prod_{n=1}^{N_{site}} s_n^{a_{nm}} + \frac{\rho_b}{\phi} K_{D,i} c_i \quad i = 1, 2, \dots, N_c.$$

Referring back to Equation 2, Equations 5 and 12 can be substituted for ψ and Ω , respectively. If we utilize an advection-dispersion operator $L(\psi) = -\nabla \cdot (\phi D \nabla \psi - v \psi)$, Equation 2 takes the form

$$\begin{aligned}
(13) \quad & \frac{\partial \phi}{\partial t} \left[\underbrace{c_i + \sum_{j=1}^{N_s} a_{ij} K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{ij}}}_{\text{Aqueous}} + \underbrace{\sum_{m=1}^{N_s} a_{im} \bar{K}_{eq,m} \exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right) \prod_{k=1}^{N_c} c_k^{a_{im}} \prod_{n=1}^{N_{site}} s_n^{a_{nm}}}_{\text{Sorbed}} + \underbrace{\frac{\rho_b}{\phi} K_{D,i} c_i}_{K_D} \right] + \\
& \underbrace{L \left[c_i + \sum_{j=1}^{N_s} a_{ij} K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{ij}} \right]}_{\text{Transport}} = 0 \\
& i = 1, 2, \dots, N_c.
\end{aligned}$$

It is this form of the governing ADR equation that we apply to simulate the solute transport and equilibrium geochemical reaction associated with subsurface sorption processes.

3. Solution Technique

GEOQUIMICO employs an operator-splitting approach to decouple Equation 13 into separate transport and reaction steps. This involves decoupling reaction from transport and computing each separately. During each time step, solute is first transported down the one-dimensional domain composed of a specified number of grid points or finite volumes. After transport, solute concentrations react locally at each node through equilibrium reaction, and the process repeats itself during subsequent time steps.

3.1 Solute Transport

Transport of component i is solved based on the governing equation

$$(14) \quad \frac{\partial(\phi\psi_i)}{\partial t} - \nabla \cdot (\phi D \nabla \psi_i - v\psi_i) = 0.$$

Notice that the total concentration (Ω) is left out of this equation since only the aqueous portion (ψ) of the total component concentration is actually transport, the sorbed portion being immobile. GEOQUIMICO provides two alternatives for transport. The first approach is to form a linear system of partial differential equations based on a standard upwind finite volume discretization of Equation 14. An alternative and more preferable approach is to decouple advection from dispersion in Equation 14, simulating advection through the more novel explicit total variation diminishing (TVD) approach with a monotonized central difference limiter (MC) (Leveque, 2002). Dispersion is then modeled using the implicit linear system of equations mentioned above. TVD improves computational efficiency and provides superior, higher-order accuracy in comparison to the first-order implicit approach mentioned above. This improved accuracy is of critical importance when modeling equilibrium chemistry along steep transport fronts since traditional methods tend to smear sharp fronts. After the linear transport step, GEOQUIMICO moves on to nonlinear geochemical reaction.

3.2 Geochemical Reaction

The geochemical reaction step involves solving for the free ion concentrations (c_i) for each chemical component. As mentioned earlier, only equilibrium reaction is currently supported by GEOQUIMICO, though kinetic formations may easily be introduced. Free ion concentrations are computed using the Newton-Raphson method, which can be viewed as a multi-dimensional Newton's method. With Newton-Raphson, a residual equation for component i is formed based on the equation for total component concentration (i.e. Equation 12).

(15)

$$f_i(c) = c_i + \sum_{j=1}^{N_s} a_{ij} K_{eq,j} \prod_{k=1}^{N_c} c_k^{a_{kj}} + \sum_{m=1}^{N_s} a_{im} \bar{K}_{eq,m} \exp\left(\frac{-\Delta z_m \Psi F}{RT_K}\right) \prod_{k=1}^{N_c} c_k^{a_{km}} \prod_{n=1}^{N_{site}} s_n^{a_{nm}} + \frac{\rho_b}{\phi} K_{D,i} c_i - \Omega_i$$

In this residual equation, (Ω_i) is held constant. Ω_i is computed by summing the total aqueous component concentration (ψ_i) obtained from the updated transport solution with the immobile

total sorbed concentration ($\bar{\chi}_i$) at each grid point i or spatial degree of freedom in the model. A Jacobian (J) is formed by computing derivatives of the residual equations (f) with respect to the chemical degrees of freedom in the system (i.e. free ion concentrations or c). To accelerate the rate of convergence for the Newton Raphson method, derivatives are often computed with respect to the natural log of the free ion concentration resulting in a better posed system, i.e.

$$(16) \quad J_{ij} = \frac{\partial f_i(c^p)}{\partial \ln c_j^p} = c_j^p \frac{\partial f_i(c^p)}{\partial c_j^p} \quad \text{for all } i, j.$$

Here, $f_i(c^p)$ is the residual equation corresponding to chemical component i (see Equation 15), computed as a function of all chemical components at that node during iteration p of Newton Raphson (i.e. vector c^p). Subscripts in J_{ij} indicate the row and column for the entry in the Jacobian.

After the linear system of algebraic equations

$$(17) \quad J \delta \ln c^p = -f(c^p)$$

is solved for vector $\delta \ln c^p$ (the change in the natural log of free ion concentration for all components resulting from the solution of iteration p of Newton Raphson), the free ion concentrations are updated individually

$$(18) \quad c_i^{p+1} = c_i^p \exp(\delta \ln c_i^p).$$

Based on double layer theory (Bethke, 1996), these updated concentrations are used to compute a new surface potential for the surface complexation reaction by solving the nonlinear relationship

$$(19) \quad \frac{F}{A_{sf}} \sum_{m=1}^{N_s} z_m \bar{X}_m = (8RT_K \epsilon \epsilon_o I \times 10^3)^{1/2} \sinh\left(\frac{z_{\pm} \Psi F}{2RT_K}\right)$$

using Newton's method. Further details regarding the explanation of variables in Equation 19 and the derivation of double layer theory may be found in Bethke (1996). The updated surface potential (Ψ) is then used to update the surface complexation reaction during the next iteration of full Newton Raphson, and this iterative process continues until the norm of residual satisfies a minimum tolerance. At that point, the free ion concentrations are stored and GEOQUIMICO moves on to the next time step.

It should be emphasized that, although the modeling of linear K_D sorption is not a demanding process, the incorporation of surface complexation is not trivial, as shown above. Surface complexation is extremely nonlinear being heavily dependent upon component and site

concentrations and surface potential, all of which are dependent upon other reactions within the system.

4. Graphical User Interface

GEOQUIMICO is written entirely in Java (i.e. J2SE 5.0). By founding the model on the extensible Java application programming interface (API), the code developer gains access to extensive libraries of ready-made software components such as GUI widgets, mathematical algorithms, and numerical solvers that facilitate programming. This approach to programming streamlines development by reducing the time spent on important, but often considered ancillary features such as the GUI. Figure 1 illustrates the main GEOQUIMICO screen. At the top of the screen, the user inputs parameters pertaining to the GEOQUIMICO transport model in text fields to the right of each label. Below these parameters, the user specifies the boundary condition type (pulse vs. continuous) and the output format (breakthrough vs. concentration profile).

All geochemical reaction parameters are specified in the middle pane where the user can select from several preconfigured geochemical scenarios or develop his/her own scenario from scratch. Within the tabbed tables, the user enters geochemical component concentrations

Geochimico

Transport Parameters

Distance (m) Velocity Number of Cells Porosity

Duration (yrs) Dispersivity Courant Criteria Soil Bulk Density

☒ Pulse Input? Pulse Duration ☒ Compute Breakthrough? Breakthrough Sampling Location

Geochemical Reaction

Pb+2 Sorption -- Kd vs. SCM Comparison

Aqueous Components Surfaces Aqueous Complexation Rxns Surface Complexation Rxns Ion Exchange Rxns Kd Rxns

Name	Init. Conc.	Type	Bound. Conc.	Type	Plot?	Color
H+	1.0E-6	Free	1.0E-6	Free	<input type="checkbox"/>	Cyan
Ca+2	7.49E-4	Free	7.49E-4	Free	<input type="checkbox"/>	Brown
Na+	8.7E-4	Free	8.7E-4	Free	<input type="checkbox"/>	Green
HCO3-	4.917E-3	Free	4.917E-3	Free	<input type="checkbox"/>	Blue
SO4-2	3.123E-4	Free	3.123E-4	Free	<input type="checkbox"/>	Magenta
Cl-	4.231E-4	Free	4.231E-4	Free	<input type="checkbox"/>	Yellow
SCM-Pb+2	1.0E-20	Free	1.0E-3	Free	<input checked="" type="checkbox"/>	Dark Blue
Kd-Pb+2	1.0E-20	Free	1.0E-3	Free	<input checked="" type="checkbox"/>	Red

☒ Compute Activities

Simulation Progress

Current Simulation (1 of 1) 100%

Total Simulations 100%

```

3995      Time: 2996.25 dt:0.75
3996      Time: 2997.0 dt:0.75
3997      Time: 2997.75 dt:0.75
3998      Time: 2998.5 dt:0.75
3999      Time: 2999.25 dt:0.75
4000      Time: 3000.0 dt:0.75
  
```

Figure 1: GEOQUIMICO main screen.

(initial and boundary) and sorption site densities along with aqueous and surface complexation reactions (formulas and equilibrium coefficients) and K_D reactions (equilibrium coefficients). Many of these parameters can be entered as random distributions for uncertainty analysis. GEOQUIMICO samples these distributions using a Latin-Hypercube algorithm and generates multiple realizations of geochemical parameters. At the right of the tables, the user toggles output options and chooses colors for plots. At the bottom of this pane, chemical components, sorption sites and reactions can be added or deleted by selecting the appropriate row in the scrollable table and clicking the button (i.e. Add or Remove) below.

The lower pane provides useful output during the simulation. Two progress bars are provided, one illustrating progress in the current realization, while the other shows progress for the entire ensemble of realizations. The lower text screen prints time step information and crucial information in the event of erroneous input or model failure. Finally, from the row of buttons at the bottom of the pane, the user starts/stops simulations and specifies the format of plot to view. The user may stop a simulation in progress if she/he so desires, though the results will be lost. Once a simulation has run to completion, plotting options (toggles, colors) may be changed and results replotted without re-running the simulations. Figure 2 illustrates GEOQUIMICO on the fly

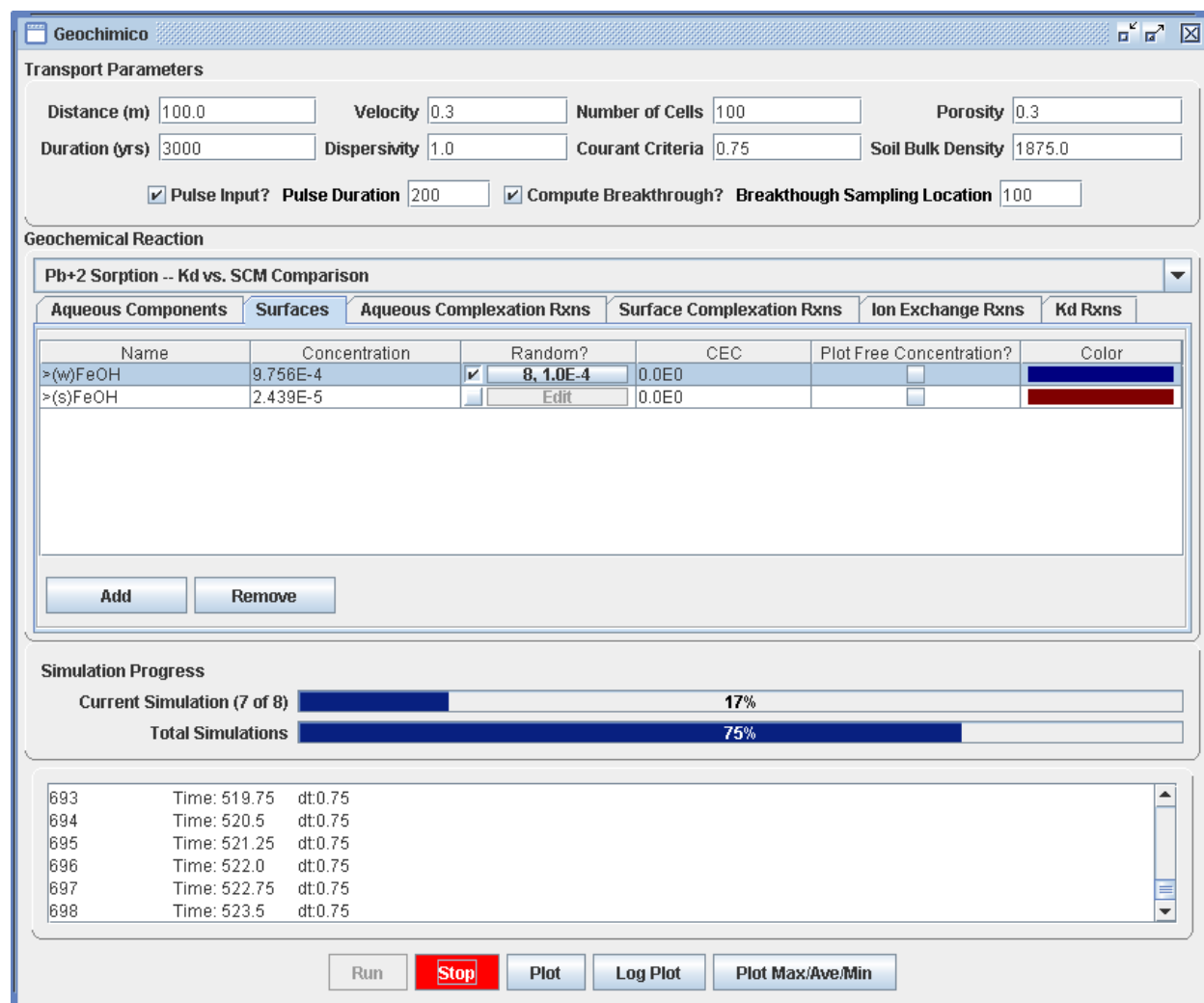


Figure 2: GEOQUIMICO model during simulation run.

where the 7th of 8 realizations is in progress. This simulation compares the K_D approach with SCM for Pb^{2+} sorption onto a mineral surface. From the highlighted line in the table under "Surfaces", one observes that the concentration for >(w)FeOH is specified as a random distribution with a mean of 9.756×10^{-4} mol/kg and standard deviation of 10^{-4} . Figure 3 presents the results of this random simulation. Notice that with a change in surface site concentration, the shape of the transport front is basically the same for SCM; however, the extent of retardation varies with higher retardation for larger site concentrations.

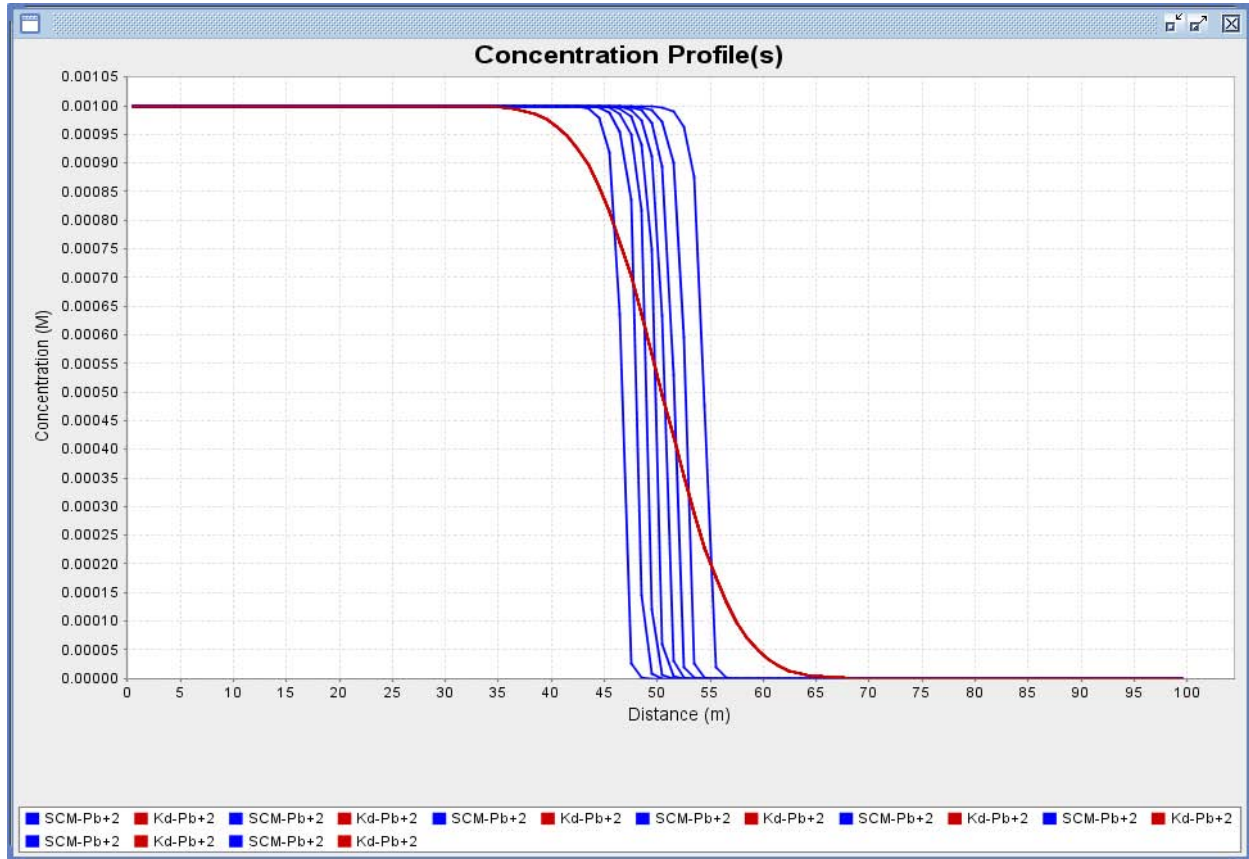


Figure 3: Pb^{2+} concentration profiles comparing the K_D solution to multiple realizations of SCM.

All plotting within GEOQUIMICO is performed using the JFreeChart library (Gilbert, 2004) which provides extensive plotting and printing capability. The user can right-click on the plot to change limits of axes, tick mark spacing, the color and font of labels/titles, etc. Plots can also be printed or saved to a portable network graphics (PNG) formatted file for viewing later.

5. Model Verification

In order to verify the accuracy of GEOQUIMICO, simulations were run using experimental data and model results presented by Bethke and Brady (2000). Although the chemical component of concern in this scenario is lead (Pb^{2+}), and not radioactive species which are of critical concern to the NRC, this exercise still serves to verify the accuracy of the surface complexation model. Simulations were run depicting the reactive geochemical transport of the components in Table 1 through a one-dimensional 100 meter column with a Darcy flow velocity of 0.3 m/yr (1.0 m/yr pore water), longitudinal dispersivity of 1.0 m, porosity of 0.3, and bulk soil density of 1875 kg/m^3 . The domain was divided up into 100 finite volumes.

Table 1: Primary chemical component concentrations (mol/L).

Component	Initial Concentration	Boundary Concentration
H^+	1.000×10^{-6}	1.000×10^{-6}
Ca^{2+}	7.490×10^{-4}	7.490×10^{-4}
Na^+	8.700×10^{-4}	8.700×10^{-4}
HCO_3^-	4.917×10^{-3}	4.917×10^{-3}
SO_4^{2-}	3.123×10^{-4}	3.123×10^{-4}
Cl^-	4.231×10^{-4}	4.231×10^{-4}
SCM- Pb^{2+}	1.000×10^{-20}	1.000×10^{-3}
K_D - Pb^{2+}	1.000×10^{-20}	1.000×10^{-3}

Note that two Pb^{2+} components are listed for the purpose of comparing the K_D approach to SCM. There is no geochemical interaction between SCM- Pb^{2+} and K_D - Pb^{2+} ; they are considered to be independent species in this scenario. Aqueous complexation reactions incorporated in this scenario are listed in Table 2 and represent buffering due to carbonate chemistry while Table 3 provides reactions for surface complexes.

Table 2: Aqueous complexation reactions.

Aqueous Complex	Reaction	Log K
OH^-	$\text{OH}^- \leftrightarrow \text{H}_2\text{O} - \text{H}^+$	-13.9951
CO_3^{2-}	$\text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- - \text{H}^+$	-10.3288
$\text{CO}_{2(\text{aq})}$	$\text{CO}_{2(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	6.3447

Table 3: Surface complexation reactions.

Surface Complex	Reaction	Log K
$>(w)FeOH_2^+$	$>(w)FeOH_2^+ \leftrightarrow >(w)FeOH + H^+$	7.29
$>(s)FeOH_2^+$	$>(s)FeOH_2^+ \leftrightarrow >(s)FeOH + H^+$	7.29
$>(w)FeO^-$	$>(w)FeO^- \leftrightarrow >(w)FeOH - H^+$	-8.93
$>(s)FeO^-$	$>(s)FeO^- \leftrightarrow >(s)FeOH - H^+$	-8.93
$>(s)FeOHCa^{2+}$	$>(s)FeOHCa^{2+} \leftrightarrow >(s)FeOH + Ca^{2+}$	4.97
$>(w)FeOCa^+$	$>(w)FeOCa^+ \leftrightarrow >(w)FeOH - H^+ + Ca^{2+}$	-5.85
$>(w)FeSO_4^-$	$>(w)FeSO_4^- \leftrightarrow >(w)FeOH + H^+ + SO_4^{2-} - H_2O$	7.78
$>(w)FeHSO_4^-$	$>(w)FeHSO_4^- \leftrightarrow >(w)FeOH + SO_4^{2-}$	0.79
$>(w)FeOPb^+$	$>(w)FeOPb^+ \leftrightarrow >(w)FeOH - H^+ + SCM-Pb^{2+}$	0.3
$>(s)FeOPb^+$	$>(s)FeOPb^+ \leftrightarrow >(s)FeOH - H^+ + SCM-Pb^{2+}$	4.65

In order to compare the two approaches to modeling sorption (i.e. K_D and SCM), a retardation of 2.0 was specified. For the K_D approach, a K_D value of 0.16 was set based on the prescribed porosity and soil bulk density values above to obtain the target retardation factor of 2.0, i.e.

$$(20) \quad R = 1 + \frac{K_D \rho_b}{\phi},$$

where ρ_b is the soil bulk density and ϕ is porosity.

Since sorbed concentrations within surface complexation are set by a mass action expression (i.e. Equation 9) instead of a simple ratio, the application of a retardation factor to SCM is less straightforward. However, for simple imbibition of a strongly sorbing solute, it is possible to approximate a retardation factor using the expression (Bethke and Brady, 2000)

$$(21) \quad R \approx \frac{s + c}{c}.$$

Therefore, by setting the sorption site concentration (s) equal to the inlet free ion concentration (c) of the sorbing ion (i.e. $SCM-Pb^{2+}$), the retardation factor becomes 2.0. Mineral surface site concentrations are shown in Table 4. Note that the sum of the sites in Table 4 equals the inlet concentration of $SCM-Pb^{2+}$ in Table 1.

Table 4: Sorption site concentrations (mol/kg mineral) for surface complexation model.

Site	Site Concentration
$>(w)FeOH$	9.756×10^{-4}
$>(s)FeOH$	2.439×10^{-5}

Simulations were run out to 3000 years. The time step size was set to 0.75 years in order to ensure minimal numerical error due to operator splitting ($CFL < 1.0$). Figure 4 illustrates concentration profiles for all primary chemical components at 100 years simulation time on a log scale. Figure 5 provides a comparison between surface complexation ($SCM-Pb^{2+}$) and the K_D approach (K_D-Pb^{2+}). Notice that SCM preserves a much sharper transport front while both

solutions exhibit the expected retardation factor of 2.0 (i.e. 50 meters traveled in 100 years based on a pore water velocity of 1 m/yr).

Figures 6 and 7 illustrate the discrepancy between SCM and K_D best. Here, breakthrough curves show that K_D does not capture the tailing effect observed with SCM, which results in concentrations well above MCLs for the duration of the simulation. These results correspond with results presented Bethke and Brady (2000) (compare Figure 7 to Figure 4 in Bethke and Brady). It should be noted that aqueous equilibrium chemistry is not explicitly defined in Bethke and Brady (2000). Through trial and error, it was discovered that the buffering of carbonate chemistry (see Table 2) was necessary to match the published result.

Although verification of the K_D approach is straightforward, further verification of GEOQUIMICO's surface complexation capability is necessary. In particular, simulations involving radionuclides of interest to the NRC need to be developed based on field observations, laboratory data, and previous modeling exercises. This will require interaction with NRC staff, licensees, and contracted researchers.

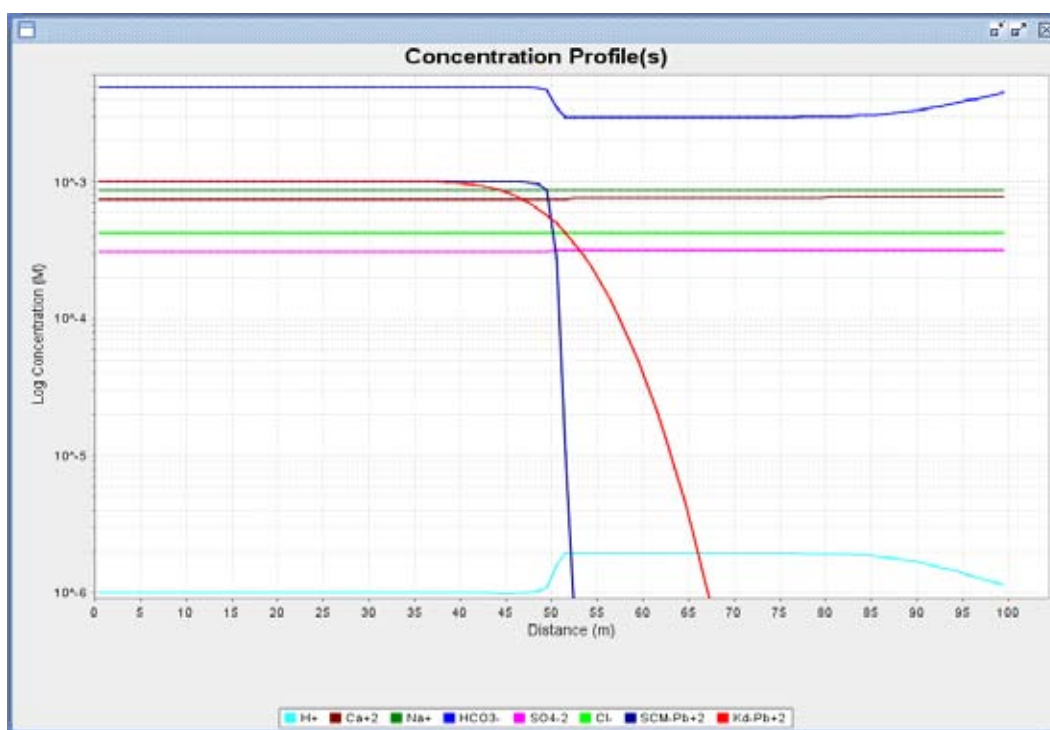


Figure 4: Concentration profiles for primary chemical components in system at 100 years simulation time.

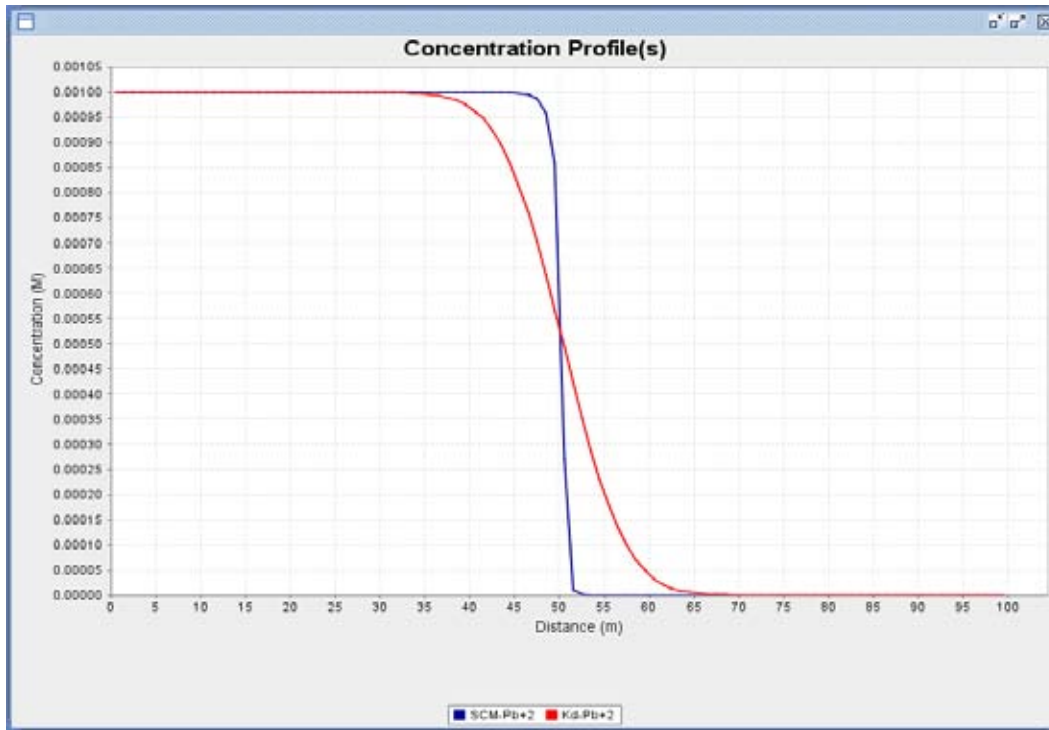


Figure 5: Comparison of SCM-Pb²⁺ versus K_D -Pb²⁺ concentration profiles at 100 years simulation time.

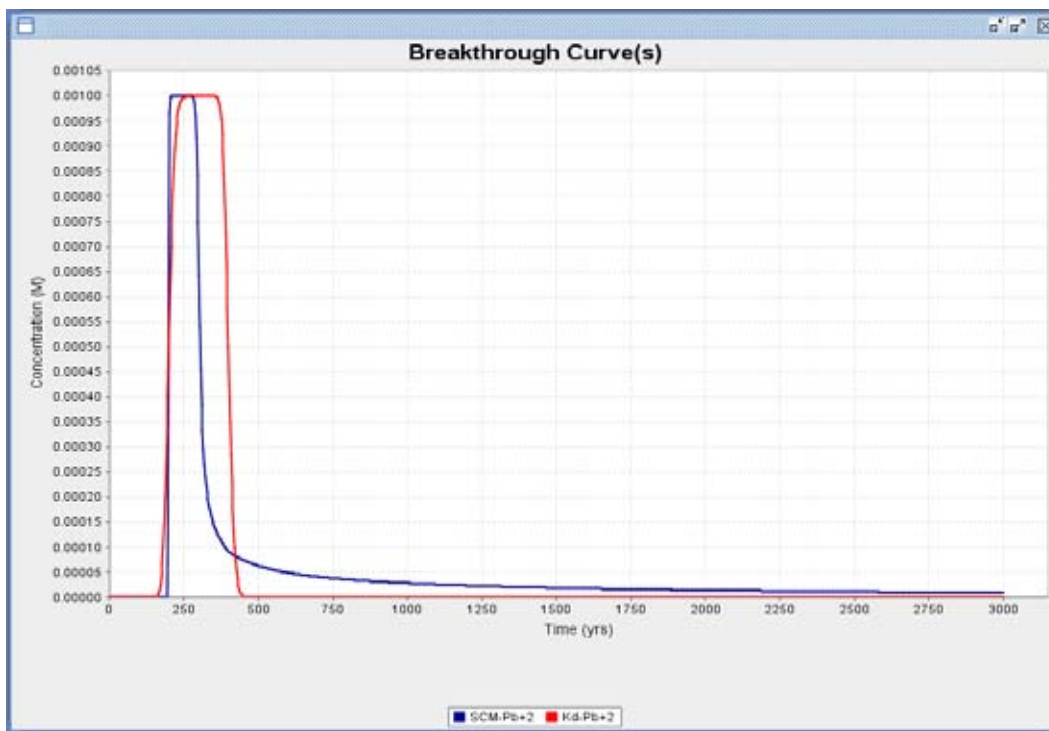


Figure 6: Comparison of SCM-Pb²⁺ versus K_D -Pb²⁺ breakthrough over 3000-year simulation.

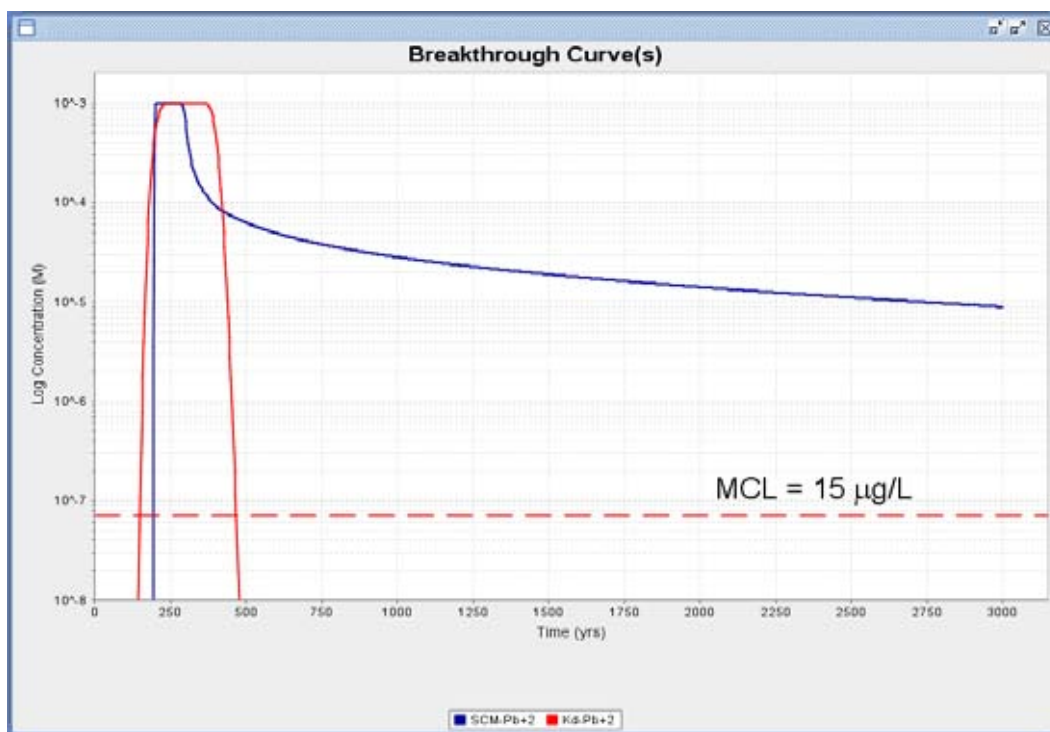


Figure 7: Logarithmic comparison of SCM-Pb²⁺ versus K_d -Pb²⁺ breakthrough over 3000-year simulation.

6. Future Directions

Development of GEOQUÌMICO to date has been primarily prototypical as a proof of concept. Although simulation results have been verified against other models and data from the literature for a select number of scenarios, additional research is still needed to verify the accuracy and performance of the code. Additionally, several key pieces of functionality need to be added to the model. Pending future funding from the NRC, the following features, critical to the success of the tool, will be added to the model:

- Ability to save/load geochemical transport scenarios to/from external files
- Improved labeling for individual realizations in plots of uncertainty (random) runs
- Statistical analysis module for reporting statistics of uncertainty runs
- Ability to sample breakthrough at multiple locations

In addition, NRC managers/staff have requested that specific capabilities be added to the model. These features include:

- Development of uranium sorption geochemical transport scenarios
- Support of non-standard distributions (e.g. log-normal) for uncertainty analysis
- Total component concentration plotting capability
- Sorption of tertiary or secondary aqueous species
- Exportation of raw data (i.e. model output) to the screen or a formatted text file

It would also be helpful to solicit feedback from NRC staff and licensees regarding needed and/or desired features in this tool. The object-oriented structure of Geoquimico, along with its Java paradigm, enables quick and efficient modification of the GUI and geochemical transport algorithms. Therefore, the model can easily be tailored to the needs of the customer whether they are NRC staff, NRC licensees, or external researchers.

7. Conclusion

The purpose of this research was to develop a user-friendly software tool for the NRC for evaluating the behavior and accuracy of sorption algorithms in modern reactive transport codes. The tool was designed to be simple for the novice reactive transport modeler to use, yet sufficiently sophisticated to accommodate complex geochemistry. Such a tool has been developed using the object-oriented Java programming paradigm, and has been named GEOQUIMICO. GEOQUIMICO is a geochemical transport code capable of modeling complex equilibrium reactions (e.g. aqueous speciation, surface complexation, linear sorption) in a one-dimensional domain. The model provides a flexible user interface for delineating transport and geochemistry input parameters and viewing simulation output. GEOQUIMICO is capable of simulating random input parameters in order to understand the sensitivity of a model result to a given parameter value. This model will facilitate the decision-making process when the use of surface complexation instead of the K_D approach is in question.

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